Phase Transition with Non-Thermodynamic States in Reversible Polymerization

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Talk, paper available from: http://cnls.lanl.gov/~ebn

SIAM Annual Meeting, San Diego, June 8, 2008
symposium: New Kinetic Models
Plan

1. Aggregation-Fragmentation Processes
2. Thermodynamic Phase
3. Nonthermodynamic Phase
4. Gelation transition
Aggregation-Fragmentation Processes

A random process in which:
small things combine to form larger things (aggregation)
and larger things break into smaller things (fragmentation)

- Chemical Physics: polymerization (Smoluchowski, Flory, Stockmeyer)
- Computer Science: random networks (Erdos, Renyi)
- Atmospheric Science: cloud formation (Drake)
- Astrophysics (Chandrasekar)
- Surface Science: Island growth (Amar)

Ubiquitous physical process
The Random Process

- **Aggregation**: merger of two small chains into a longer chain
  \[ [i] + [j] \xrightarrow{K_{ij}} [i + j] \]
  ![Aggregation Diagram]

- **Fragmentation**: breakage of a large chain into smaller chains
  \[ [i + j] \xrightarrow{F_{ij}} [i] + [j] \]
  ![Fragmentation Diagram]

- Process is perfectly reversible when rates are non-zero
  \[ K_{ij} \neq 0 \quad F_{ij} \neq 0 \]

- Initial Condition: N monomers \( c_k(t = 0) = \delta_{k,0} \)

- Goal: find the steady-state size distribution
The Master Equation

- Describes the evolution of the size distribution

\[
\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j \geq 1} K_{kj} c_j + \sum_{j \geq 1} F_{kj} c_{j+k} - \frac{1}{2} c_k \sum_{i+j=k} F_{ij}
\]

- Provides exact description when:
  
  - System is infinite (thermodynamic limit)
  - System is perfectly mixed (no spatial correlations)

Implicitly assumes size distribution is finite!
(number of chains of size k is proportional to N)
Equilibrium Steady-States

- Steady-state size distribution satisfies

\[ 0 = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j \geq 1} K_{kj} c_j + \sum_{j \geq 1} F_{kj} c_{j+k} - \frac{1}{2} c_k \sum_{i+j=k} F_{ij} \]

- Solve by equating aggregation and fragmentation fluxes

- Detailed balance condition

\[ K_{ij} c_i c_j = F_{ij} c_{i+j} \]

- Fluxes between any two states of the system balance

- Example: constant rates yield an exponential distribution

\[ \begin{align*}
K_{ij} &= r, \\
F_{ij} &= 1
\end{align*} \implies c_k \propto r^k \]

When do equilibrium solutions exist?
Detailed Balance Condition

- Detailed balance condition
  \[ K_{ij} c_i c_j = F_{ij} c_{i+j} \]

- For example, take \( k=1,2,3,4 \)
  \[ \begin{align*}
    K_{11} c_1^2 &= F_{11} c_2 \\
    K_{12} c_1 c_2 &= F_{12} c_3 \\
    K_{13} c_1 c_3 &= F_{13} c_4 \\
    K_{22} c_2^2 &= F_{22} c_4
  \end{align*} \]

- Solution exists only when rates satisfy the condition
  \[ \frac{K_{12}}{F_{12}} \frac{K_{13}}{F_{13}} = \frac{K_{11}}{F_{11}} \frac{K_{22}}{F_{22}} \]

- Detailed balance equation over-determined

- An infinite set of conditions on the rates

Generically, steady-state is nonequilibrium in nature
Product aggregation + constant fragmentation

- **Aggregation**: Constant reaction rate between any two monomers
  
  random network (erdos-renyi)
gelation (flory-stockmayer)

- **Fragmentation**: breakage of a large chain into to smaller chains
  
  polymer degradation (ziff)

- **Master equation**

  \[ 0 = \frac{1}{2} \sum_{i+j=k} ij c_i c_j - kc_k + \lambda \sum_{j > k} c_j - \frac{\lambda}{2} (k - 1)c_k \]

- **Detailed balance condition violated**

  \[ \frac{K_{12}}{F_{12}} \neq \frac{K_{11}}{F_{11}} \frac{K_{22}}{F_{22}} \]

  Nonequilibrium steady-state
I. Thermodynamic Phase
   (strong fragmentation)
Strong Fragmentation \((\lambda > 1)\)

- Moments of the size distribution
  \[
  M_n = \sum_{k=1}^{\infty} k^n c_k
  \]

- Total density of clusters is finite when \(\lambda > 1\)
  \[
  M_0 = 1 - \lambda^{-1}
  \]

- Cluster size distribution is finite for all \(k\)
  \[
  c_1 = \frac{\lambda - 1}{\lambda + 1}, \quad c_2 = \frac{(\lambda - 1)(3\lambda + 1)}{(\lambda + 1)^2(3\lambda + 4)}
  \]

- Large clusters are exponentially rare \((\text{from generating function})\)
  \[
  c_k \sim k^{-5/2} e^{-\text{const} \times k}, \quad k \to \infty
  \]

1. Finite density, number of clusters proportional to \(N\)
2. Many small clusters, few large clusters
3. Total density of clusters vanishes as \(\lambda \to 1\) ???
Near critical behavior \((\lambda = 1 + \epsilon)\)

- Perturbation analysis, small parameter \(\epsilon = \lambda - 1\)

\[
C_k = \epsilon b_k
\]

- Nonlinear convolution term irrelevant, linear equations

\[
k b_k = \sum_{j=k+1}^{\infty} b_j - \frac{1}{2} (k - 1)b_k
\]

- Explicit linear recursion

\[
\frac{b_{k+1}}{b_k} = k - \frac{1}{3}
\]

\[
b_k \propto \frac{\Gamma(k - \frac{1}{3})}{\Gamma(k + \frac{4}{3})}
\]

- Power-law size distribution over a diverging scale

\[
c_k \sim \epsilon k^{-5/3} \quad k \ll \epsilon^{-3}
\]

1. Fewer small clusters, more large clusters
2. Nonlinear convolution term becomes irrelevant
II. Nonthermodynamic Phase
(weak fragmentation)
Sub-critical behavior \( (\lambda < 1) \)

- **Nonlinear convolution term is irrelevant, linear equations**
  \[
  k c_k = \lambda \sum_{j=1}^{k-1} c_j - \frac{\lambda}{2} (k - 1) c_k
  \]

- **Power-law size distribution, exponent varies**
  \[
  c_k \sim k^{-\beta} \quad \beta = \frac{2 + 3\lambda}{2 + \lambda} \quad 1 < \beta < \frac{5}{3}
  \]

- **Mass conservation dictates system size dependence**
  \[
  c_k \sim N^{\beta-2} k^{-\beta}
  \]

- **Total number of clusters grows sub-linearly!**
  \[
  N_{\text{tot}} \sim N^\gamma \quad \gamma = \frac{2\lambda}{2 + \lambda} \quad 0 < \gamma < \frac{2}{3}
  \]

Nonthermodynamic state! number of clusters is not proportional to system size \( N \)
Thermodynamics vs. Nonthermodynamic states

• **Strong fragmentation: thermodynamic state**
  - Total density is finite
  - Total number of clusters is proportional to $N$
  - Many small clusters

• **Weak fragmentation: nonthermodynamic state**
  - Total density decays with system size
  - Total number of clusters grows slower than $N$
  - Few large clusters

Dramatic consequence of nonequilibrium dynamics
Microscopic vs Macroscopic Clusters

- Strong fragmentation: sizes on a finite scale
- Weak fragmentation: sizes on all scales
  - Macroscopic clusters ("gels") exist
  - Macroscopic clusters contain finite fraction of mass

Master equations do not involve $N!$
Monte Carlo Simulations

- Master equations “know nothing” about $N$
- Monte Carlo simulations involve $N$
- Sub-linear behavior causes slow convergence

Power law size distribution

Sub-linear number of clusters

Simulations confirm the theoretical predictions

$M \sim N^{2/5}$
Cascade

- **Balance of two fluxes of mass**
- **Aggregation**: transfers mass from small to large scale
- **Fragmentation**: transfers mass from large to small scales

\[
N^\gamma \quad (k/N)^{-\beta} \quad N \quad c_k
\]

- **fluid turbulence** (kolmogorov)
- **wave turbulence** (zakharov)
- **advection** (falkovich)
- **granular matter** (ebn, machta)
Dynamics: gelation transition

- Moments diverge at a finite time
  \[ M_n \sim (t_g - t)^{-(n-1)} \]
  \[ \frac{dM_n}{dt} = \frac{1}{2} \sum_{m=1}^{n-1} \binom{n}{m} M_{m+1} M_{n+1-m} - \frac{\lambda}{2} \frac{n-1}{n+1} M_{n+1} \]
  \[ + \frac{\lambda}{n+1} \sum_{m=2}^{n} \binom{n+1}{m} B_m M_{n+1-m} \]

- Finite time singularity

- Power-law size distribution (balance aggregation & fragmentation fluxes)
  \[ c_k \sim k^{-2} [\ln k]^{-1} \]

- The size of the nucleating gel is nearly macroscopic
  \[ k_g \sim N [\ln N]^{-1} \]

- Second relaxation relaxation step
  \[ \tau \sim \ln N \]

Two stage dynamics
Compare with classic gelation

<table>
<thead>
<tr>
<th></th>
<th>moments</th>
<th>size distribution</th>
<th>critical gel size</th>
</tr>
</thead>
<tbody>
<tr>
<td>aggregation-fragmentation</td>
<td>$M_n \sim (t_g - t)^{-(n-1)}$</td>
<td>$c_k \sim k^{-2}[\ln k]^{-1}$</td>
<td>$k_g \sim N[\ln N]^{-1}$</td>
</tr>
<tr>
<td>aggregation</td>
<td>$M_n \sim (t_g - t)^{-(2n-3)}$</td>
<td>$c_k \sim k^{-5/2}$</td>
<td>$k_g \sim N^{2/3}$</td>
</tr>
</tbody>
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Qualitatively different critical behavior
Summary

• Nonequilibrium phase transition

• Strong fragmentation: thermodynamic phase
  - Number of clusters proportional to system size
  - Few large clusters (exponential tail)

• Weak fragmentation: nonthermodynamic phase
  - Number of clusters much smaller system size
  - Many large clusters (powerlaw tail)
  - Macroscopic clusters exist, contain finite fraction of mass
  - Finite time singularity: macroscopic clusters nucleate
  - Giant fluctuations (macroscopic size)
Outlook

- Master equations 2.0
- General theory of nonequilibrium steady-states
- Dynamics beyond the gelation point
- Finite-size scaling near the phase transition point

\[ N_{\text{tot}} \sim \begin{cases} 
  C(\lambda) \frac{N^{2/3}}{\lambda \uparrow 1} \\
  (\lambda - 1)N \quad \lambda \downarrow 1 
\end{cases} \]

Chayes, Balobas, et al 01 ebn, krapivsky 05